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NITROGEN IN TITANIUM CARBIDE AND
TITANIUM-WOLFRAM ALLOYS

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Mintsvetmetzoloto
Inst of Hard Alloys

[A Digest]

Production of titanium hard alloys has been considerably developed in recent years. However, practical achievements are far ahead of investigations in the field of metallography and technological processes of these essential alloys. Certain questions on the structure of alloys and its effect on properties remain unanswered. The effect of separate admixtures on the sintering process and on final properties of the alloys has not been investigated.

The main difficulty in manufacturing titanium alloys is obtaining titanium carbide of a standard and satisfactory quality. The problem is complicated by the fact that there has been no clarification of the composition of titanium carbide which is satisfactory for obtaining alloys of good quality.

Under production conditions titanium carbide is prepared by heating a mixture of titanium dioxide with carbon black in carbon-tubular resistance furnaces at 1900-2200° in a hydrogen atmosphere. The content of combined carbon in the carbides thus obtained varies from 17.5 to 19% and does not reach the 20 percent corresponding to the formula for TiC. Deficient carbon atoms in the lattice of titanium carbide are replaced by atoms of oxygen and nitrogen and, thus, the product of carburization represents a solid solution of Ti(C, O, N). This is in complete agreement with the similarity between crystal lattices of titanium carbide (TiC), titanium nitride (TiN), and titanium oxide (TiO).

Such a concept of titanium carbide is developed in the works of G. A. Meyerson [4] and Ya. S. Umanskiy [5].

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The presence of nitrogen in the carbide is explained by the difficulties of hermetically sealing the furnace. A certain small amount of air is always sucked into the furnace and causes nitriding of the carbide and its decarburization.

Investigations of the carburizing reaction of titanium, conducted by G. A. Meyerson and Ya. M. Lipkes [6, 7], demonstrated that the reaction has three stages in conformity with the existence of the three titanium oxides: $TiO_2 \rightarrow Ti_2O_3 \rightarrow TiC \rightarrow TiC$.

The authors assume that the last stage of the reaction in the temperature range of 1700-2500 does not reach completion because of the greater stability of the solid solution $TiC-TiO$ formed in this stage.

In addition, it was established that maximum saturation with carbon (19-19.5%) is achieved during the initial stage of the reaction, and further, that the carbon content comes down to 16-17%. Such a decrease in the content of combined carbon is explained mainly by the interaction of nitrogen, present in the gas atmosphere of the furnace, with the titanium carbide.

Until recently it has been assumed that the chief cause of the difficulty in sintering titanium-wolfram alloys is the presence of oxygen and nitrogen in titanium carbide [7, 8].

The main defect of sintered products is a "porous core." Its formation is explained by the escaping of oxygen (in the form of CO) and nitrogen from the alloy during the sintering process, when recrystallization of carbide grains proceeds through the liquid phase formed by the binding metal.

In the sintering process, first of all, gases escape from outer layers of the product, and quick shrinkage and compression occurs in these layers, hampering separation of gases from deeper layers, which causes swelling and the porous core of the product.

The sintering process proceeded quickly and quite satisfactorily if a carbide of theoretical composition with the minimum content of impurities was used for alloying. This factor indirectly confirmed the negative role of nitrogen and oxygen. However, no investigations have yet been conducted to study the effect of oxygen and nitrogen, taken separately, on the sintering process.

The purpose of this work was the more detailed investigation of the nitriding process of titanium carbide and influence of the nitrogen content in carbide on the sintering process, structure, and properties of alloys.

A series of experiments was conducted to study the process of nitriding the titanium carbide in an atmosphere of hydrogen, a mixture of hydrogen with nitrogen, and pure nitrogen. Data obtained permits the following conclusions.

When titanium carbide is held in the furnace with a pure dry hydrogen atmosphere, decarburization of carbide occurs. This process is caused, depending on temperature, by the oxidizing or nitriding action of small amounts of sucked-in air which cannot be avoided completely.

There is mainly an oxidizing action at 1200° ; nitriding is practically absent at this temperature. The oxygen content increases with time and reaches 25% by weight. The sum of $N+C$ combined + O in experiments at 1200° exceeds 50 at %, indicating the presence of oxides higher than TiO , such as Ti_2O_3 .

It must be taken into consideration that the oxidizing agent in this case appears to be carbon monoxide, which reacts at 1200° with carbide according to the formula: $2TiC + 3CO = Ti_2O_3 + 5C$.

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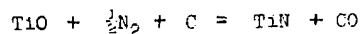
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At 1400° the nitriding process begins, in addition to oxidizing action. The oxygen content decreases as the product continues to remain in the furnace, while the amount of nitrogen increases (from 0.74 to 4%). Consequently, the nitriding process partially proceeds via the displacement of oxygen with nitrogen:



Simultaneously, probably, nitriding proceeds according to the reaction $2\text{TiC} + \text{N}_2 + \text{H}_2 = 2\text{TiN} + \text{C}_2\text{H}_2$, and partially according to $\text{C}_2\text{H}_2 = 2\text{C} + \text{H}_2$.

At 1800°, chiefly the nitriding action of sucked-in air is in effect. Oxidation at this temperature is negligible. A regularity may be better observed here for the decrease in oxygen in respect to the length of holding time (from 2.7 to 0.38%) with simultaneous increase in the nitrogen content (from 2.3 to 7%). The sum of $\text{N} + \text{C} + \text{O}$ for all experiments at 1800° is 50 at % or lower.

Analysis of decarburization products proved the lack of equivalence between increases of nitrogen and free carbon in products of the reaction. The equivalence might take place if the nitriding should proceed only according to the reaction: $2\text{TiC} + \text{N}_2 = 2\text{TiN} + 2\text{C}$.

Actually, at high temperatures displaced carbon is partially bonded with hydrogen into hydrocarbons. This assumption was confirmed by experiments with pure nitrogen. In the absence of hydrogen, the increase of free carbon and nitrogen is very near to equivalence.

Essential practical conclusions may be drawn from the experiment conducted. At high carburizing temperatures (1900-2000°) the sole agent for decarburizing the titanium carbide is nitrogen. Oxidation of the carbide at these temperatures is not observed even with a furnace period of up to 9 hrs. Hence, the presence of oxygen in industrial carbides is the result of a reaction which was not completed. With a short furnace period carbides more saturated with carbon may be obtained, but they contain oxygen. With prolonged soaking periods the nitriding process begins with simultaneous further displacement of remaining oxygen. As a result of this procedure, the carbide obtained is less saturated with carbon, contains some nitrogen but is almost completely free of oxygen. This may explain the composition of certain industrial carbides which often contain nitrogen and are free from oxygen.

For studying the influence of nitrogen in titanium carbide on the sintering process, structure, and properties of alloys it was necessary to prepare a series of carbides differing only in their nitrogen contents and having practically no oxygen. The easiest way to obtain such carbides is to mix at various ratios specially nitrided carbide with that of low nitrogen content.

Titanium carbide with a definite percentage of nitrogen was mixed with wolfram carbide at a ratio corresponding to their contents in an alloy of the Ti_{15}W_6 type (15% TiC , 79% WC , and 6% Co). Metallic wolfram was introduced into the mixture for binding free carbon. After heating the mixture of carbides at 1,650° in a hydrogen atmosphere, the solid solution of wolfram carbide in titanium carbide was formed.

Analysis of these double carbides shows that additional nitriding occurs in the process of forming the solid solution if the nitrogen content is low (up to 0.3%). With a higher nitrogen content, some denitriding takes place.

Double carbides obtained were mixed after crushing with powdery cobalt in steel drums with balls for 24 hrs. Plates 5 x 5 x 35 mm were pressed out of these mixtures under pressure of 1.5 tons/cm². Sintering of plates was executed under industrial conditions for $\text{Ti}_{15}\text{W}_6\text{C}$ alloys with application of graphite protective powder and in a hydrogen atmosphere. The carbon boat with specimens was continuously moved through the furnace (1530° for 1.5 hrs).

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Alloys thus obtained were thoroughly investigated. Chemical analysis was conducted, specific gravity, hardness, and bending strength were determined, the microstructure of the alloys was studied, and, in conclusion, tests of cutting qualities were conducted.

It was established that nitrogen, within the range of contents up to 1%, does not separate out of alloys during sintering but remains in the carbide solid solution and therefore has no harmful effect on the sintering process or on the hardness and toughness of the alloys.

It was also established that nitrogen does not lower the cutting properties of alloys which contain up to 1.3% nitrogen.

Thus, the results of the investigations lead to the conclusion that nitrogen is not a harmful admixture and that there are more reasons to consider oxygen a harmful impurity.

Investigations conducted permit some suggestions essential for production: The quality of titanium carbide may be controlled by the sum of carbon, nitrogen, and titanium. Absence or low content of oxygen may be accepted as the criterion of carbide quality. It is necessary to choose those conditions for carburization of titanium which will permit removal of a maximum amount of oxygen. There are no reasons to consider the nitriding of titanium carbide as a harmful factor, at least in the range of up to 1% nitrogen content in an alloy.

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